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ABATEMENT OF CORROSION
IN
CENTRAL HEATING SYSTEMS

BY

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ABATEMENT CORROSION IN CENTRAL HEATING SYSTEMS.

By F. N. Speller.

INTRODUCTION.

This paper is published by the Bureau of Mines as a contribution to the literature on the corrosion of iron and steel and as a guide to engineers in the design of heating systems.

Whether hot water or steam is used as the medium for conveying heat to the consumer, a heavy toll in upkeep must be faced sooner or later if the corrosion of piping is not taken into account in the design of the plant. The main source of corrosion has been traced to dissolved gases brought into the heating system either with the feed water for the boiler or through leaks in return lines under a pressure below that of the atmosphere.

PIPE MATERIAL.

In practice the piping must be of either wrought iron or steel. Both have their advocates, but both are inherently sensitive to the action of hot water. This sensitiveness varies according to conditions that are discussed on another page. The basis for trade arguments claiming that some kinds of iron pipe are practically immune to corrosion should be carefully investigated, for it has been well established that the factors which cause corrosion, rather than any commercial difference in the composition of the pipe, determine the rate of corrosion. Moreover, records of a considerable number of comparative service tests, conducted by independent and reliable investigators, of the corrosion of pipe carrying hot water indicate practically no difference, on the whole, among reputable makes of wrought iron and steel pipe. This phase of the problem need not be considered further, for even if some kind of pipe had, say, 30 per cent longer life and cost 30 or 40 per cent more, the engineer would not gain by increasing the first cost of the plant in this way. On the other hand, if by good engineering design, at some slight additional expense, he could eliminate the main source of the trouble, the extra investment would probably seem more attractive. The cost of the pipe is of course only a small percentage of the cost of renewals, which must be taken into account in figuring the value of auxiliary apparatus to minimize corrosion.

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THEORY OF CORROSION.

The following abstract from a recent paper by Speller and Knowland[a] gives an outline of the fundamental reaction of corrosion in the light of our present knowledge of the subject:

> With reference to corrosion it is possible to classify any particular water under one of two types which may be distinguished by the terms *active* and *inactive*. The quality of activity is not primarily dependent upon the acid, alkaline, or neutral condition of a water, but rather upon certain dissolved substances which exert a modifying influence upon the universal tendency of even the purest water to initiate the corrosion process. This inherent tendency of pure water to attack metal may be greatly aided in those cases where dissolved gases exist in the liquid, and under such conditions the term active typifies its corrosive qualities. An inactive water is one that is not able to promote in any marked degree the corrosion of iron. The sharp boundary between the behavior of these two types of water furnishes a sufficient reason for thus distinctively classifying them. It is a simple matter to demonstrate the fact that an inactive water, after a few minutes aeration, becomes capable of great damage to iron.
>
> Every metal, when placed in water is subjected to a certain fixed tendency to go into solution. This effect is wholly a matter of electrochemical activity and varies to a definite extent with each metal. The initial reaction in the process of corrosion of iron by water is exactly analogous to its solution in acid. Water exists in the liquid state not only in the form of its molecule, but also as *ions*. These are formed by the breaking up or dissociation of the molecule and some carry a charge of positive electricity, and some a negative charge. This condition has been represented pictorially in figure 1, *A*. All water is broken up in this way although the proportion actually so dissociated is extremely minute. Acids, like water, are ionized, but to a far greater extent into hydrogen ions and those formed from the remainder of the acid molecule. The net result of the presence of an acid in water is, therefore, to increase the amount of positively charged hydrogen ions present. It is the concentration of these hydrogen ions in water that determines its ability to attack iron; indeed, the initial speed of attack is proportional to the number of hydrogen ions in the water. It is thus easily understood that, while pure water with its very low concentration of acid ions is capable of inducing the corrosion of iron, water containing an acid will be proportionately more ruinous to the metal. It is, therefore, a fact that the *tendency* of iron to corrode depends to a certain degree upon the amount of acid present in the surrounding water. We shall show that corrosion, however, may be arrested even in a distinctly acid water. With this in view, too much emphasis can not be laid upon the fact that we must recognize two definite conditions under one of which water acts as a corrosive liquid, whereas under the other it is harmless to metal.
>
> If we place a piece of iron in water, a multitude of tiny electrolytic cells are immediately established. The currents flow through the ionized water from point to point upon the surface of the metal, these points often being distinguished by the presence of surface impurities, an irregularity of finish, or some similar unusual condition. In figure 1, *B*, the initial stages of corrosion are illustrated as occurring with the appearance of these currents. The direction of movement of the ions formed by the dissociation of the water should be particularly noted. A positively charged ion will always be attracted toward a negative surface, while the negative ions move in an opposite direction.

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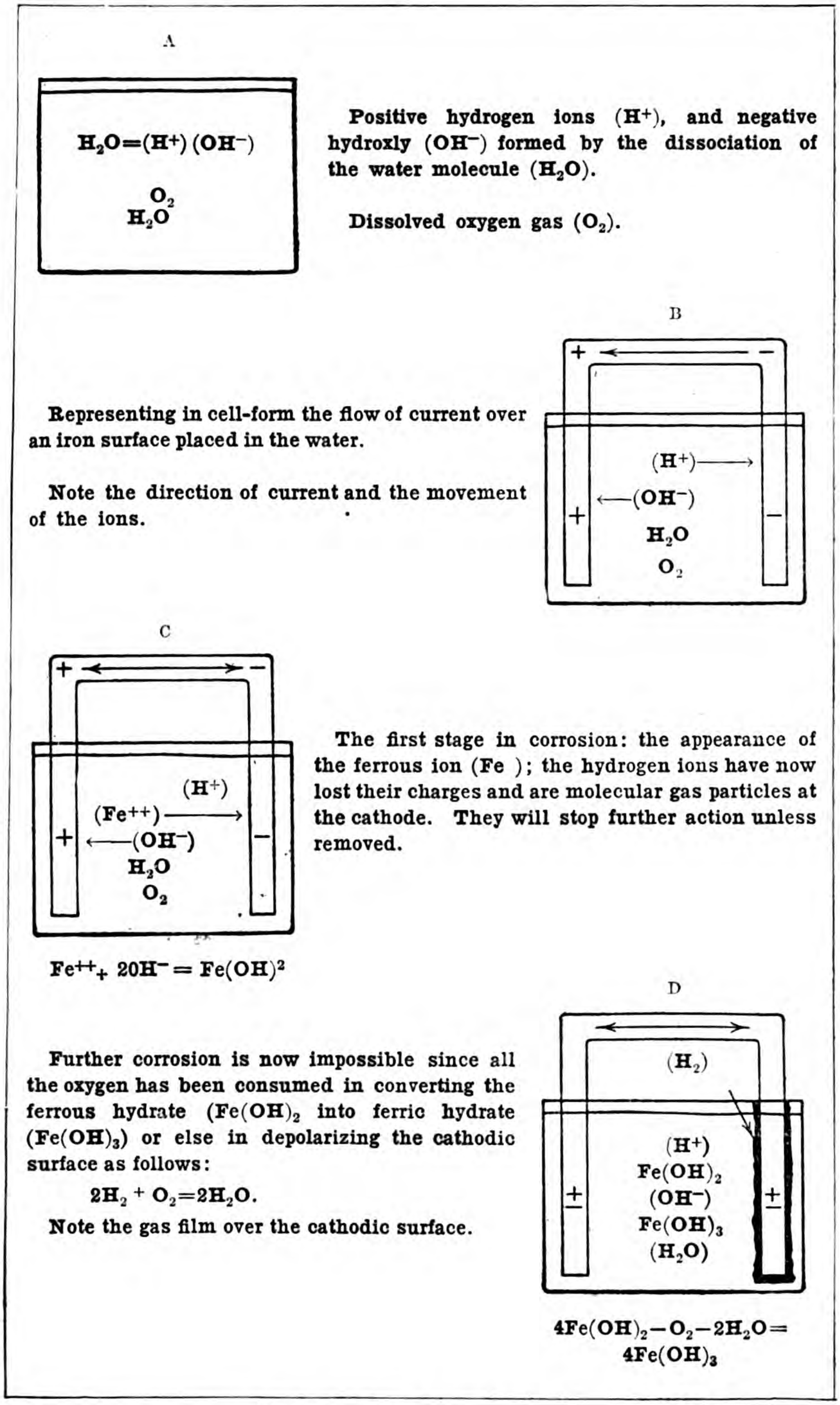
[a] Speller, F. N., and Knowland, R. G.: Preservation of hot-water supply pipes in theory and practice. Proc. Am. Soc. Heat. and Vent. Eng., vol. 24, 1918., pp. 217–240.



Positive hydrogen ions (H^+), and negative hydroxly (OH^-) formed by the dissociation of the water molecule (H_2O).

Dissolved oxygen gas (O_2).

Representing in cell-form the flow of current over an iron surface placed in the water.

Note the direction of current and the movement of the ions.

The first stage in corrosion: the appearance of the ferrous ion (Fe); the hydrogen ions have now lost their charges and are molecular gas particles at the cathode. They will stop further action unless removed.

$$Fe^{++} + 2OH^- = Fe(OH)^2$$

Further corrosion is now impossible since all the oxygen has been consumed in converting the ferrous hydrate ($Fe(OH)_2$ into ferric hydrate ($Fe(OH)_3$) or else in depolarizing the cathodic surface as follows:

$$2H_2 + O_2 = 2H_2O.$$

Note the gas film over the cathodic surface.

$$4Fe(OH)_2 - O_2 - 2H_2O = 4Fe(OH)_3$$

Figure 1.—Process of corrosion of pipe.

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The actual destruction of metal begins as shown by figure 1, *C*. Here the current previously established is removing metallic iron from the anode surface, and sending it into solution in the form of its ions, each of these bearing two charges of positive electricity which cause its passage toward the nearest negative surface or cathode. Its progress is soon arrested, however, as it meets the negatively charged hydroxyl ions moving in the opposite direction. These two ions combine, their charges neutralize each other, and ferrous hydrate is formed. The appearance of ferrous hydrate and hydrogen marks the first external evidence of corrosion.

Meanwhile, the positively charged hydrogen ions have reached a negative surface, being neutralized there and forming hydrogen gas molecules. These molecules unite with any oxygen present to form water, otherwise, they collect over the cathodic surface, ultimately preventing further flow of current or "polarizing" it and ending the activity of corrosion by an actual congestion of its processes. It should be noted that the presence or absence of oxygen in this way determines the possibility for corrosion. Thus, an *inactive* water may become extremely corrosive or *active* upon being aerated.

In figure 1, *D* is illustrated the final stage of rusting, where all the dissolved oxygen has disappeared from the water. Note that the ferrous hydrate is partly oxidized to ferric hydrate or rust. The layer of hydrogen on the cathodic surface has finally become so dense that the current is completely polarized and no further corrosion will be possible until it has been removed. It thus becomes apparent that the presence of dissolved oxygen in no sense causes corrosion, but merely aids in its unimpeded operation. And this holds true whether the water is pure or acidic.

While dissolved oxygen is usually the factor determining the rate of corrosion, attention must be called to another phase of the problem. This involves a phenomenon called the discharge potential of hydrogen. Briefly stated, when water is decomposed by an electric current, a certain difference of potential is required for the discharge of hydrogen upon the cathode, and this voltage depends upon the kind of cathode in question. If the potential required for the discharge of hydrogen is greater than that available, the gas will accumulate about the cathodic portions of the metal, and, unable to discharge, will soon polarize the process of electrolysis. Since the solution of iron in water is purely an electrochemical phenomenon, as had been demonstrated, these effects must be considered as applying strictly to every individual case of corrosion. Although the potential difference required for the discharge of hydrogen upon a metal is a very small quantity, a fraction of a volt, which may even be negative in value, the very low voltage obtained from the ionization of iron in water may not in every case be sufficient to compel such an effect. But if salts be present in the water, the metallic element of which can be plated on the cathodic surfaces by the current, it is evident that the nature of the metal deposited will raise or lower the discharge potential and hence determine whether electrolysis shall continue or shall cease—in other words, whether corrosion may occur.

As an extreme case, we may mention arsenic compounds which are well known to act in preventing the corrosion of iron. This effect is due to the fact that arsenic is deposited over the cathodic spots. The discharge potential of hydrogen on arsenic is too high to be overcome by the feeble current resulting from the corrosion process, hence, this is retarded by the presence of an arsenic salt. Copper salts, on the other hand, promote corrosion owing to the low discharge potential of hydrogen upon this metal.[a] The important point to be kept in mind is the fact that corrosion is purely a matter of electrolytic activity, that it is stopped by polarizing the cathode surfaces by any means available, and that the nature of the cathode surfaces of itself is able to aid or to hinder corrosion. These effects and their bearing upon the solution of metals in acids, are admirably discussed in the paper by Watts and Whipple[a], which was presented this year before the American Electrochemical Society.

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[a] It is obvious that if a powerful current from external sources be impressed upon a metal surface, the discharge potential of hydrogen may be exceeded many times, when an extremely rapid loss of metal will result. Herein, we find the cause for the disastrous effects of the "stray" currents that so often, in a very short time, completely ruin piping installations.

The influence of the discharge potential upon corrosion is often of paramount importance; but in the majority of cases of severe corrosion inside pipe lines, with only iron in contact with water and no metallic salts present, the cause of the trouble is associated only with oxygen gas dissolved in the water. We have no positive proof that corrosion can be promoted by carbon dioxide or by any other similar gas if oxygen is not present. It is true that the presence of carbon dioxide, since it causes acidity, always implies a tendency toward corrosion, but if oxygen is not present also the possibilities for corrosion are very slight. All our experimental evidence goes to show that the minute current involved in the rusting of iron is too feeble by itself to overcome the polarization resulting from this process. Hence, continued corrosion will be impossible unless oxygen or some metal or salt is present to take care of the hydrogen film that builds up in the path of the current. It is very evident that oxygen is the usual depolarizer met with in ordinary waters, and that we must therefore consider the presence of this gas to be the key to the vast majority of cases of corrosion of iron and steel. If oxygen can be eliminated from water, with the effect of rendering the latter *inactive*, corrosion in pipes, tanks, boilers, and in other similar places may be practically prevented. We have no evidence upon which to base a belief that the acidity of a water modifies such a general conclusion.

Thus we see why corrosion is promoted and made progressive and continuous by the action of dissolved oxygen in water.

When the supply of oxygen ceases the reaction rapidly slows down, as all the available free oxygen is used in depolarizing the surface or in combining with ferrous hydrate. In the end the water is "deactivated" in the sense that it has been rendered practically inert to metals.

THE ENGINEERING PROBLEM.

Pipes for hot-water heating in buildings do not suffer seriously from corrosion if the same water is circulated repeatedly through the pipes, but if a considerable proportion of make-up water is put into the system the corrosion becomes rapid, especially in districts such as New York City or New England, where the water is comparatively soft.

Under such conditions, when considerable water is used, hot-water supply pipes of galvanized wrought iron and steel frequently fail by perforation after seven or eight years' service. In a study of this problem, the author found some systems using open heaters wherein the water was allowed to come to rest several minutes at a temperature of 180° F. or higher, thus discharging the bulk of the gases. Pipe used under these conditions showed practically no corrosion after 10 years' service.

In a hot-water supply system arranged as in the old system in figure 1, the oxygen rapidly decreased as the water passed from the heater and storage tank through the system and back to the storage tank through the return. In this circuit the water lost about 90 per cent of its oxygen content. To a similar system, figure 2, was attached a storage tank filled with expanded steel lathing, and a filter to clarify the water. In this system practically all the free oxygen is removed in the storage tank. After three years under these conditions there was practically no corrosion in the pipes carrying this "deactivated" water. On the average the deactivation was not over more than 95 per cent complete. This illustrates the cause of this trouble and an inexpensive remedy which can be applied to hot water supply systems.

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[a] Watts, O. P, and Whipple, N. D. The corrosion of metals in acids: Proc. Am. Electro-Chem. Soc., vol. 32, 1917, pp. 257-284.

Free carbon dioxide is present in this water and is not reduced by the treatment, therefore in the absence of oyxgen, as there is no noticeable action of the water on the pipe, it must be concluded that the effect of CO_2 is negligible in such a system. In more concentrated solutions, such as the condensate in steam return lines, free CO_2 might be a factor. Should this be found to hold, the boiler feed water may be treated with lime or barium hydrate to fix the free carbonic acid.

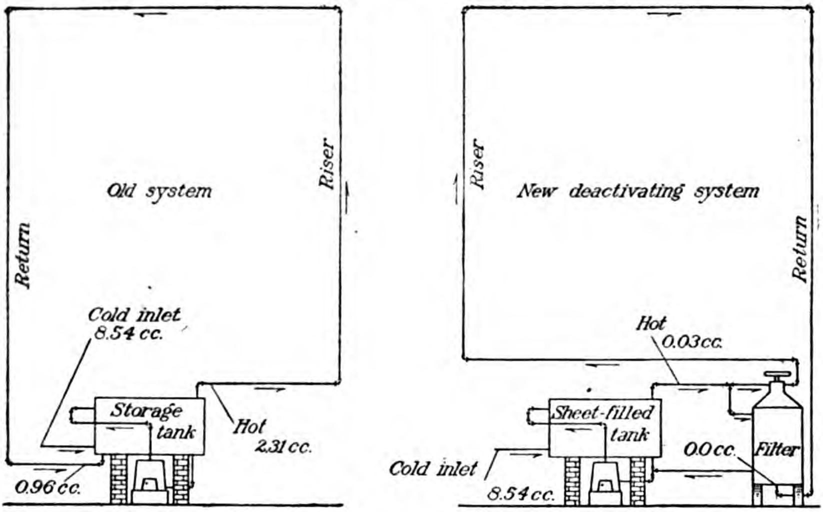

FIGURE 2.—Corrosion and noncorrosion in heating systems.

In effect, a steam-heating system is a large-sized air-cooled condenser. Any non-condensable gases in the feed water are reabsorbed by the condensate and may cause serious corrosion, especially along the bottom of horizontal lines. In large central district power plants it may be more economical to remove the gases from feed-water by using well-designed open heaters or some other form of air remover. Open heaters alone, when handling large volumes of water, usually do not remove enough of the gases but the residual oxygen may be removed by the use of steel sheet, as illustrated in figure 2, A. In a properly proportioned plant large quantities of hot water may be deaerated in this way at reasonable cost. Of course there may be some air leakage in steam returns; this should be avoided as much as possible. Determinations of free oxygen are comparatively easy to make and may be used to detect air leakage.

Where exhaust steam from reciprocating engines is used, a coating of oil usually forms on the inside of the return pipes and protects the metal considerably. In adopting such protection, care should be taken to use a pure mineral oil, preferably one with a paraffin base.

Such treatment was applied successfully in one of the stations of the Duquesne Light Co., Pittsburgh, Pa., to a steam turbine that was corroding seriously around the blades. This turbine had to be stopped for six hours every day, and during that time condensation occurred. The condensed water in the presence of oyxgen that entered with the steam or through leakage started corrosion. This went on intermittently for about two years, when the damage became serious. Having in mind the protection afforded by oil deposited in steam returns, the author suggested that, as a temporary expedient, some pure heavy mineral oil with a paraffin base be dropped into the steam ahead of the throttle at a regular rate. As a result a thin coating was deposited on the casing and blades. This casing gave good protection, one and one-half gallons of oil a day producing the best results. At intervals of two or three weeks the turbine was opened for inspection, and the amount of oil used was regulated by the condition of the coating. The engineers in charge add about one and one-half gallons of kerosene on shutting the turbine down every day and five gallons every Saturday night before the weekly shutdown. The kerosene cleans out any deposits that have collected between the blades.

Although with proper control this oil treatment will probably protect against corrosion it is not so good, of course, as removal of the source of the trouble.

Much remains to be learned as to the engineering refinements involved in the removal of gases from water and as to how much must be done to assure immunity from corrosion in pipes; but enough has been accomplished to enable an engineer to trace out and remove from water the free oxygen that is undoubtedly the main cause of corrosion.

PUBLICATIONS ON CORROSION.

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Technical Paper 15. An electrolytic method of preventing corrosion of iron or steel, by J. K. Clement and L. V. Walker. 1913. 19 pp., 10 figs.

Technical Paper 58. Action of acid mine water on the insulation of electrical conductors, a preliminary report, by H. H. Clark and L. C. Ilsley. 1913. 26 pp., 1 fig.